

RECEIVED  
CENTRAL FAX CENTER

OFFICIAL

JUN 24 2004

PATENT

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Wang et al.

Application No. 10/036,332

Filed: Dec. 24, 2001

For: CARBON NANOTUBE  
CONTAINING STRUCTURES,  
METHODS OF MAKING, AND  
PROCESSES USING SAME:  
:  
:  
:  
:  
:  
:  
:  
:  
:

Art Unit: 1724

Examiner: R. Hopkins

Atty Docket: 12860E-CIP

DECLARATION PURSUANT TO 37 CFR § 1.131

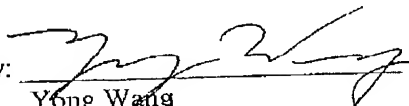
1. The attached document in which the first line reads "Prepare two kinds of samples:" is a copy of six lab notebook pages that were all written by Yufei Gao before 20 September 2000. These notebook pages contain descriptions of experiments that were carried out before 20 September 2000.

2. As indicated on the third line of the first page, a goal of this work was to prepare a structure of CoRu/Al<sub>2</sub>O<sub>3</sub> particles on carbon nanotube sponge grown on mesoporous SiO<sub>2</sub>/Fe/Al<sub>2</sub>O<sub>3</sub> dense coating/stainless steel foam.

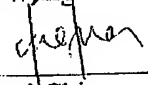
3. The second page of the attachment shows an early experiment in which a coating of carbon nanotubes ("CN") was deposited on a stainless steel foam.
4. The sixth (and last) page of the attachment shows the successful synthesis of composite structures that included carbon nanotubes on a stainless steel foam.
5. The stainless steel foams used in this work had large pores and these foams had through porosity. The stainless steel foam had a pore size of more than 100 nm.
6. All of the attached documents have been copied without change except that dates have been blanked out.
7. The work in the attached notebook pages is that of Yufei Gao. At the time of the work described in the attached notebook pages, Dr. Gao was working with Yong Wang.
8. Claim 6 of the pending application states:  
A porous carbon nanotube containing structure comprising:  
a large pore support having through porosity; and  
carbon nanotubes disposed over the large pore support.  
Yufei Gao and Yong Wang are joint inventors of claim 6. Ya-Huei Chin, Christopher L. Aardahl, and Terry L. Stewart are not joint inventors of the subject matter of claim 6.

9. I declare that all of the above statements made of my own knowledge are true and all statements made on information and belief are believed to be true. I understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. §1001), and may jeopardize the validity of the application or any patent issuing thereon.

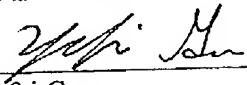
Date: 5/18/04

By:   
Yong Wang

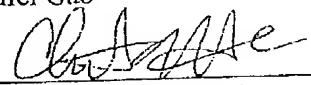
Date: 5/19/04

By:   
Ya-Huei Chin

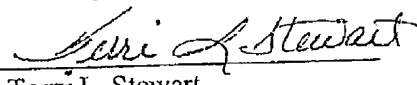
Date: 5/12/04

By:   
Yufei Gao

Date: 5/21/04

By:   
Christopher L. Aardahl

Date: 5/21/04

By:   
Terry L. Stewart

Using Colloid  $Al_2O_3$  particles to coat carbon nanotubes

- Carbon nanotubes / metal foam

↳ surf. area:  $\sim 1000 \text{ m}^2/\text{g}$

Three small pieces

#1, #2 - etching in 50% H<sub>2</sub>SO<sub>4</sub> / 50% H<sub>2</sub>O<sub>2</sub> for 10 min at room temp.

⇒ hydrophilic

#1 sample:

dip in 20%  $Al_2O_3$  solution (original one)

#2 sample:

dip in 50% ethanol / 50% - 20%  $Al_2O_3$  solution

#3 sample:

No chemical etching

dip in 20%  $Al_2O_3$  solution

SEM image:

It appears that there is a dense layer on top of the CN film.  
#1 & #2 samples have some cracks on the dense layer, &  
#3 sample has a high density of cracks - due to the hydrophobic nature?

It is not clear how much  $Al_2O_3$  inside the CN film for #1 & #3.

SEM shows a lot of  $Al_2O_3$  on CN tubes in the CN film for sample #3.

Note: Samples made on Tue.

Project No. \_\_\_\_\_ Date of Work \_\_\_\_\_  
Entered By Qiao, Yue Fei, All Date \_\_\_\_\_  
Disclosed To and Understood By \_\_\_\_\_

42

Try to dilute the  $Al_2O_3$  solution more in order to coat the CN films.

- #1 sample (small)  
etching in 50%  $H_2SO_4$  / 50%  $HNO_3$  for 10 min at RT  
Dip in 3:1 Ethanol : 20%  $Al_2O_3$  solution
- #2 sample (big)  
etching in 50%  $H_2SO_4$  / 50%  $HNO_3$  for 10 min at RT  
Dip in 4:1 Ethanol : 20%  $Al_2O_3$  solution

Both were sec. dried okay

SEM (old one, new one also not working)  
Both small & big samples still have a dense coating layer. SEM can't tell whether there is any  $Al_2O_3$  in the CN film due to poor resolution

⇒ Should I wash the sample in  $H_2O$  / EtOH after dip coating the  $Al_2O_3$  to remove any excess  $Al_2O_3$  particles on the top of CN films?

Note:

1) New SEM shows ~~that~~ no dense layer on top of the CN films

2) It appears that 4:1 dilution is better. Next I will try much we deposit on ~~one~~ CNs or in CN films

Project No. \_\_\_\_\_ Date of Work \_\_\_\_\_  
Entered By Gao, Yue Fei Date \_\_\_\_\_  
Disclosed To and Understood By \_\_\_\_\_  
Signed 1. [Signature] Date \_\_\_\_\_  
2. [Signature] Date \_\_\_\_\_

44

- Coat Co, Ru on  $Al_2O_3$  / CN / Foams:
- Try to coat the foams in #2 Co/Ru solution  
 $\Rightarrow$  too much  
 or at thickness? *test*
  - Samples:  
 Two Colloid  $Al_2O_3$  / Foams (small & big)  
 One CVD Si:  $Al_2O_3$  / Foam
  - Initial weight & weight gain:  
 CVD:  $0.0246 \rightarrow 0.0261 = 0.0015$  g or 6%  
 big (4:1):  $0.0316 \rightarrow 0.0348 = 0.0032$  or 10%  
 small (3:1):  $0.0175 \rightarrow 0.0194 = 0.0019$  or 10%  
 } after Vac. Drive
  - SEM  
 CVD:  
 most CNs are still individual, & coatings are quite uniform (Co/Ru). CNs inside the films appear smaller in diameter.  
 Without Si during, the  $Al_2O_3$  coating maybe just exist.  
 Photo: L1211-1  $\Rightarrow$  -8
  - Big (4:1):  
 Co/Ru /  $Al_2O_3$  coatings appear very uniform (1st step)  
 Small  $Al_2O_3$  particles (random diameter) also fill the space between CNs (at least on out surface). Small pores can be ~~observed~~ observed. L1215-1  $\Rightarrow$  -4
  - Small (3:1):  
 The Co/Ru /  $Al_2O_3$  coatings appear not as dense as the big (4:1)  
 Large pores are clearly visible. L1214-1  $\Rightarrow$  -7
  - The difference bet big & small may be due to the size effect.  
 For small piece, the excess solution can be easily removed

Project No. \_\_\_\_\_ Date of Work \_\_\_\_\_

Entered By Gao, Yue Fei, M Date \_\_\_\_\_

Disclosed To and Understood By \_\_\_\_\_

Signed 1. [Signature] Date \_\_\_\_\_2. [Signature] Date \_\_\_\_\_

Prepare the kinds of samples:

- 1) CoRu / Al<sub>2</sub>O<sub>3</sub> mesoporous coating / Al<sub>2</sub>O<sub>3</sub> dense coating / SS foam
- 2) CoRu / Al<sub>2</sub>O<sub>3</sub> particles / Carbon monolith sponge / mesoporous Al<sub>2</sub>O<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> dense coating / SS;

- First Al<sub>2</sub>O<sub>3</sub> dense coatings on SS foam  
4 Monoliths of SS foams from Wayne (this morning)

Al<sub>2</sub>O<sub>3</sub> coatings:

- 700°C growth temperature
- 102°C Al bubbler temperature (84%) } took 3 hrs to stabilize
- 151°C line temperature (56%) }
- Heating to 700°C in 500 sccm N<sub>2</sub>, 5°C/min
- growth:
  - Air - 500 sccm,
  - Al carrier: 30 sccm 5.8% output
  - 20 min growth time
  - 5 Torr

- cooling down to RT (off power) in N<sub>2</sub>

initial weight:

0.2800 g	0.2601 g	Flan ←
0.2858 g	0.2602 g	

After grow:

0.2800 g	0.2601
0.2820 g	0.2611
gain 0.0020 g	0.0010 g
0.2858	0.2602
0.2872	0.2622
0.0014 g	0.0020 g

- Al<sub>2</sub>O<sub>3</sub> mesoporous coatings

Solution #1

1.5 g H<sub>2</sub>O, 4 g EtOH, 0.08 g HCl, 1 g C<sub>16</sub>E<sub>4</sub>O<sub>10</sub>, 1.0 g Al<sub>2</sub>O<sub>3</sub>  
⇒ did not use because of H<sub>2</sub>O!

Solution #2

3.5 g EtOH, 0.08 g HCl, 1 g C<sub>16</sub>E<sub>4</sub>O<sub>10</sub>, 1.0 g Al<sub>2</sub>O<sub>3</sub>  
0.2622 → 0.2700 ⇒ 0.0078 g gain ⇒ looks good!

Solution #3

5 g EtOH, 0.25 g P123, 0.8 g Al<sub>2</sub>O<sub>3</sub>  
0.2820 → 0.2984 ⇒ 0.0164 g ⇒ too much on surface!  
↳ too much ⇒ due to P123!

Calcined  
at 500°C  
for 1 hr  
500 Torr,  
1000 sccm Air

Project No.

Date of Work

Entered By

Date

Disclosed To and Understood By

Date

26

Cali

- Carbon Nanotube Seed layer  
Solution #4

1.5 g H<sub>2</sub>O, 4 g EtOH, 0.08 g HCl, 2 g C<sub>60</sub>, 4 ml 7.  
Two mmol/liter:

Calcium  
at 500°C  
for 1 hr  
in 1000 scum  
500 Torr

0.2611 → 0.2720 ⇒ 0.0109 g } Both look quite uniform, no  
0.2872 → 0.2976 ⇒ 0.0104 g } error on the surface

Also:

dip coating ~ 10 small foams coated with Ag<sub>2</sub>S<sub>2</sub>O<sub>8</sub> previously.  
Most are use. Others

⇒ see some bubbles on the external surface, which were  
absent without Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O

Two dried on a hot plate ⇒ more bubbles on the surface

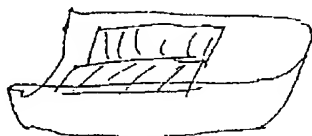
Also coated ~ 10 flat SS samples

- Carbon Nanotube growth

done

Flame

→



#2 see SEM images  
L125B-1, -2

500 scum N<sub>2</sub> atmosphere

350°C/hr → 750°C 500 scum N<sub>2</sub>

at 750°C, 900 scum ethylene for 5 min ⇒ 300 scum for 25 min

350°C/hr → RT, 500 scum N<sub>2</sub>

⇒ Too much Carbon Nanotubes!

I used wrong time, lost time

10 min, not 30 min!

⇒ Carbon Nanotubes almost completely filled the pores!

growth time also

Weight gain:

0.2858 g → 0.2872 → 0.2976 → 0.003 → 0.1437 CN

From

CO<sub>2</sub>

Fe/SiO<sub>2</sub>

CN

⇒ almost complete filled

Project No.

Date of Work

Entered By

Gao, Yue Fei

Date

Disclosed To and Understood By

Signed 1.

Date

2.

Date

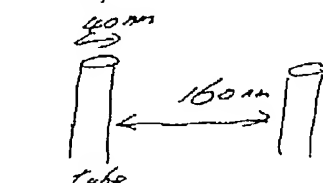


Conti

27

-  $Al_2O_3$  particle Deposition on Carbon Nanotubes  
 Solution method:

$$AlCl_3 \quad \rho = 2.44 \text{ g/cm}^3$$



$$\text{Solution vol.} = \pi(100^2 - 20^2) \cdot 1 = 9600 \pi$$



or Filled with solution

$AlCl_3$  coating  $\delta$  - thickness

$$\text{Thus, } 10\% \text{ } AlCl_3 \text{ in solution: } 2\pi r \delta \cdot 1 = 40\pi \cdot \delta$$

$$9600\pi \cdot 10\% = 40\pi \cdot \delta \Rightarrow \delta = \frac{96}{4} = 24 \text{ nm}$$

Making 10 wt.%  $AlCl_3$  in EtOH:

5 ml EtOH

$$10\% \rightarrow 0.5 \text{ ml } AlCl_3 \rightarrow 0.5 \times 2.44 = 1.22 \text{ g } AlCl_3$$

When mixing  $AlCl_3$  in 5 ml EtOH, generating a lot of heat! The glass bottle was hot.

This was done in the fume box.

Notes:

The solution was stirred over water and with the cap closed

$\Rightarrow$  very thick colloidal solution, why?

- forming Al ethoxide?  $Al(O_2C_2H_5)_3$  particles?

Making a TEM sample, diluting the colloidal solution by a factor of ~2 (4 ml EtOH)

$\Rightarrow$  completely dissolved, no precipitations!  
 No TEM samples.

Take out 4 ml solution, & add 0.6 g  $Al_2O_3 \Rightarrow \sim 10\%$

thickness  
to reach!

$\Rightarrow$  colloid! add all EtOH: 9 ml at  $1.22 + 0.6 = 1.82 \text{ g } AlCl_3$

Project No. \_\_\_\_\_ Date of Work \_\_\_\_\_

Entered By Gao, Yue Fei Date \_\_\_\_\_

Disclosed To and Understood By \_\_\_\_\_

Signed \_\_\_\_\_ Date \_\_\_\_\_